Title: **Multifunctional (NO_x/CO/O_2) Solid-State Sensor for Coal Combustion Control**

Author: Eric D. Wachsman
Materials Science and Engineering
University of Florida
Gainesville, FL 32611-6400
352-846-2991
352-846-0326
ewach@mse.ufl.edu

Grant No: DE-FG26-02NT41533

Performance: 09/30/02 – 06/07/05

Objective(s):
There is a tremendous environmental and regulatory need for the monitoring and control of NO_x and CO emissions from coal combustion sources. We have developed solid-state sensor technology that can provide an inexpensive, rugged, solid-state device capable of measuring the concentration of multiple species (such as NO and CO) in coal combustion exhaust. Our goal is to extend this technology to create a single potentiometric (voltage output) sensor that is sensitive to multiple gasses (NO_x, CO, O_2). Such a sensor can be used to improve combustion control, resulting in both improved fuel utilization and reduced emissions.

Our sensors are based on the same technology used in conventional automotive O_2 sensors and thus can be used directly in high temperature exhaust. In our design, all the electrodes are in the same gas stream, significantly reducing fabrication cost. The main obstacle in developing and commercializing low-cost, solid-state, electrochemical sensors for emissions monitoring is attaining the necessary gas selectivity. Specifically, the sensors must exhibit a highly selective response to ppm levels of NO_x and CO in the presence of percent levels of O_2.

The operation of our sensors, that provides the necessary selectivity of NO even in lean-burn (13-17% O_2) exhaust gas, can be explained through a scientific approach we developed called "Differential Electrode Equilibria". By this theory, a difference in electrochemical potential between two electrodes exposed to the same environment will occur if one or both of the electrodes does not achieve thermodynamic equilibrium. In a potentiometric sensor this non-Nernstian response produces a voltage that depends on the concentration of one or more of the species present.

Accomplishments to Date:
We investigated the effect of electrode microstructure and showed that small particle size, high surface area, electrodes increased sensor sensitivity. We fabricated and tested sensors with both n-type and p-type metal oxide electrodes. These sensors showed high sensitivity and selectivity towards NO, CO and NO_2. The voltage response of the n-type electrode is opposite in sign to that of the sensor with the p-type electrode, consistent with our "Differential Electrode Equilibria" mechanism. Similarly, and as expected by this mechanism, the reducing gas (NO) and the oxidizing gas (NO_2) also exhibit opposite voltage responses.

The sensing mechanism was further elucidated using temperature programmed desorption (TPD) and reaction (TPR). The results showed that co-adsorption of gasses results in a complex surface species. In addition, these results showed that the minimum sensor operating temperature is due to saturation of the electrode surface with adsorbed gasses, further confirming our “Differential Electrode Equilibria” mechanism.

Future Work:

Further study of the properties of these sensors, including electrode geometry, thickness, and porosity are planned for further optimization of the electrode performance. Future work also involves developing electrodes with improved selectivity towards CO, NO_2, and O_2. Once this is achieved, work will be focused on creating a multifunctional sensor that utilizes each of these electrodes.

Presentations:

“Differential Electrode Equilibria: A More Comprehensive Potentiometric Sensor Mechanism,” The National Academies (USA) and The Science Council of Japan Workshop on the Future of Sensors and Sensor Systems, February 28-March 2, 2005, Tsukuba, Japan.

“Evaluation of Metal Oxide Sensing Behavior with Respect to Adsorption/Desorption Behavior,” American Ceramic Society, January 24-28, 2005, Cocoa Beach, FL

“Selectivity and Cross-sensitivity of NO Gas sensing Elements in Combustion Exhaust,” American Ceramic Society, January 24-28, 2005, Cocoa Beach, FL

“Studies of Influence of Adsorption and Catalytic Reaction of Gas Sensing Properties of a Potentiometric Sensor,” American Ceramic Society, January 24-28, 2005, Cocoa Beach, FL

“Differential Electrode Equilibria: A More Comprehensive Potentiometric Sensor Mechanism,” American Ceramic Society, January 24-28, 2005, Cocoa Beach, FL

"Selective Potentiometric Detection of NO_X by Differential Electrode Equilibria," E.D. Wachsman, 202nd Meeting of The Electrochemical Society, October 20-24, 2002, Salt Lake City, UT.

“Yttria Stabilized Zirconia Based Potentiometric Sensors for NO_x,” E.R. Macam, 27th Annual International Conference & Exposition on Advanced Ceramics & Composites, January 27-31, 2003, Cocoa Beach, FL.

“Yttria Stabilized Zirconia Based Potentiometric Sensors for NO_x,” E.R. Macam, University Scholars Symposium, University of Florida, April 12, 2003,Gainesville, FL.

“Yttria Stabilized Zirconia Based Potentiometric Sensors for NO_x,” E.R. Macam, 105th Annual Meeting & Exposition of The American Ceramic Society, April 27-30, 2003,Nashville, TN.

"Catalytic and Electrocatalytic Reduction of NO_x on $LaBO_3$ Surfaces,"E.D. Wachsman -Keynote Lecture, NATO Advanced Research Workshop on Mixed Ionic Electronic Conducting Perovskites for Advanced Energy Systems, June 1-5, 2003, Kiev, Ukraine.

"Multifunctional (NO_x/CO/O_2) Solid-State Sensor for Coal Combustion Control", E.D. Wachsman, The 2002 NETL Sensors and Control Program Portfolio Review and Roadmaping Workshop, October 15-16, 2002, Pittsburgh, PA.

Publications and Patents:

“Selective Potentiometric Detection of NO_X by Differential Electrode Equilibria,” E.D. Wachsman, Journal of the Electrochemical Society, submitted.

“Selective Potentiometric Detection of NO_X by Differential Electrode Equilibria,” E.D. Wachsman, Solid State Ionic Devices III, Electrochem. Soc., E.D. Wachsman, K.S. Lyons, M. Carolyn, F. Garzon, M. Liu, and J. Stetter, Ed., 2002-26, 215 (2003).

"Solid State Potentiometric Gaseous Oxide Sensor," E. D. Wachsman and A. Azad, July 29, 2003, U.S. Patent No. 6,598,596.

Students Supported:

Jiho Yoo, Suman Chatterjee, Briggs White, Eric R. Macam, Jun-Young Park, and Martin van Assche